1991

NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA IN HUNTSVILLE

COMPUTERIZED REDUCTION OF ELEMENTARY REACTION SETS FOR COMBUSTION MODELING

Prepared by: Carl V. Wikstrom, Ph.D.

Academic Rank: Assistant Professor

Institution: University of Arkansas
Mechanical Engr. Dept.
Fayetteville, AR

NASA/MSFC:

Laboratory: Propulsion
Division: Propulsion Systems
Branch: Performance Analysis

MSFC Colleague: Charles F. Schafer, Ph.D.
Klaus W. Gross

Contract No.: NGT-01-008-021
The University of Alabama
in Huntsville

1. Introduction

Modeling of chemistry in Computational Fluid Dynamics can be the most time-consuming aspect of many applications. If the entire set of elementary reactions is to be solved, a set of stiff ordinary differential equations must be integrated. Some of the reactions take place at very high rates, requiring short time steps, while others take place more slowly and make little progress in the short time step integration.

Historically, the problem has been approached in several ways:

1) Single Step - Instantaneous Reaction: While computationally simple, this technique will over-predict conversion since the equilibrium point will be surpassed.

2) Total Equilibrium: This is the assumption used in ODE and TDE at MSFC. The assumption may be adequate in describing the overall performance of an engine, but may fail to provide the detail required for the spatial resolution which CFD analysis is to provide. That is, the assumption may not be valid for the local conditions resulting from the CFD calculations.

3) Reduced Mechanism - Finite Rate: The choice of the appropriate reduced set is difficult, since the local conditions are not constant throughout the CFD calculations. Since the importance of the elementary reactions may change within the computational space, the global set chosen may not be appropriate for the local conditions.

4) Partial Equilibrium - Finite Rate: A portion of the reactants are assumed to be in equilibrium, while the remainder are integrated in finite rate kinetics. This approach removes the very short time step calculations and allows integration of fewer equations at longer time steps. Since there is an interaction between the equilibrated and non-equilibrated species, an equilibrium calculation is performed at each time step. KIVA (Los Alamos) utilizes this approach. However, the proper choice of equilibrated and non-equilibrated reactions may change with the local conditions.

The goal of this work is to develop a procedure to automatically obtain sets of finite rate equations, consistent with a partial equilibrium assumption, from an elementary set appropriate to local conditions. The sets can be applied to the appropriate regions within the CFD space where the total equilibrium assumption is inappropriate.

2. Approach

The full elementary set of equations was solved for a single cell using CHEMKIN (Kee, et al, 1989) and PSR (Glarborg, et al.,

1986). It was necessary to assign each reaction as equilibrated, frozen (no reaction occurring), or finite rate. The assignment was made as follows:

Let the characteristic reaction time be defined as:

$$\tau_{rxn} \equiv \frac{C_t}{R_i}$$

Where $C_t \equiv$ Total molar concentration (moles/cm^3)
and $R_i \equiv$ Molar reaction rate (moles/c^3-s) for equation i.

and the characteristic residence time as:

$$\tau \equiv \frac{\dot{m}}{\rho V}$$

Where $\rho \equiv$ Density (g/cm^3)
$V \equiv$ Volume of cell (cm^3)

and $\dot{m} \equiv$ mass flow rate into cell (g/s).

Then the assignment was made as follows:

$$\frac{\tau_{rxn}}{\tau} > 100 \qquad \textit{Frozen}$$

otherwise the reaction was classified as not frozen. The value of 100 was arbitrary and may be changed in future applications. The frozen reactions and the species appearing only in the frozen reactions were discarded.

Let R_f indicate forward direction reaction rate and R_r indicate reverse reaction rate and R_{max} indicate the greater of the forward and reverse rate. The following criterion was used for equilibrated designation:

$$\frac{|R_f - R_r|}{R_{max}} < 0.05 \qquad \textit{Equlibrated}$$

The species appearing in the equilibrated reactions were assumed to be in partial equilibrium (reactants with products).

The remainder of the reactions were classified as finite rate and were retained. The partially equilibrated species were used to further reduce the finite rate mechanism using the method outlined by Chen (Chen, 1988).

3. Test Case

The hydrocarbon portion of the Miller/Bowman (Miller, et al., 1989) mechanism was used for the development of the procedure. This elementary reaction set contains 151 reaction and 33 species.

The conditions chosen were:

$$\dot{m}=47kg/s \quad P=212.7atm. \quad V=41.48l$$

$$Feed\ Volume\ Fractions: \quad C_2H_4\ 0.306 \quad O_2\ 0.694$$

The resulting residence time is 1.3 ms.

Of the 151 reactions in the elementary reaction set, 79 were frozen and were discarded. 43 reactions were equilibrated and 29 were designated finite rate. The 29 finite rate reactions contained 20 species, 13 of which were equilibrated in the set of 43 reactions. These reactions were further reduced to the following set of "global" reactions:

1. $O_2 + 2C \rightharpoonup 2CO$

2. $2O_2 + C + 3CH \rightharpoonup 3CO + CH_2OH$

3. $C + C_2H_4 \rightharpoonup CH + C_2H_3$

4. $O_2 + C + C_2H_4 \rightharpoonup CH + CO + CH_2OH$

5. $CH + CO \rightharpoonup HCCO$

6. $2CH + CO \rightharpoonup C + CH_2CO$

7. $O2 + C + CH + HCCO \rightharpoonup CH_2 + 3CO$

Note that the Miller/Bowman mechanism was assembled for the purpose of modeling NO_x formation and C_1 hydrocarbons are important in "prompt" NO formation. The current approach should be able to maintain accurate prediction of C_1 concentrations, which would be lost in a total equilibrium approach, by using only the above global mechanism and a partial equilibrium assumption on the remaining species.

4. Conclusions and Future Work

The possibility of computerized reaction reduction has been demonstrated. However, the ability to use the reduced reaction set depends on the ability of the CFD approach in incorporate partial equilibrium calculations into the code. Therefore, the results should be tested on a code with partial equilibrium capability.

The predictive capability of the resulting reduced set is can be no better than that of the original elementary reaction set. The procedure should also be tested on other elementary reaction sets.

The current test was at conditions on the scale of a full combustion chamber. Testing of the procedure at the conditions of an individual cell is appropriate.

Under certain conditions, multiple sets of partially equilibrated species may result. The current procedure should be modified to facilitate multiple sets of partially equilibrated species.

5. References

Chen, J-Y, "A General Procedure for Constructing Reduced Reaction Mechanisms with Given Independent Relations", Combustion Science and Technology, 1988, Vol. 57, pp. 89-94.

Glarborg, P., Kee, R.J., Grcar, J.F., and Miller, J.A., "PSR: A Fortran Program for Modeling Well-Stirred Reactors", Sandia Report SAND86-8209, UC-4, February, 1986.

Kee, R.J., Rupley, F.M., and Miller, J.A., "Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics", Sandia Report SAND89-8009, UC-401, September, 1989.

Miller, J.A. and Bowman, C.T., "Mechanism and Modeling of Nitrogen Chemistry in Combustion", Progress in Energy and Combustion Science, 1989, Vol. 15, pp. 287-338.